Clay composites as ballistic witness materials: time, temperature, and history dependent material properties[1]

J.E. Seppala[1], Y. Heo[2], C.R. Snyder[1], K.D. Rice[3], G.A. Holmes[1]

[1]*Materials Science and Engineering Division, National Institute of Standards and Technology, 100 Bureau Dr., Gaithersburg, MD 20899, USA, jonathan.seppaala@nist.gov*
[2]*Montgomery College, Gaithersburg, MD 20899, USA*
[3]*Materials Measurement Science Division, National Institute of Standards and Technology, 100 Bureau Dr., Gaithersburg, MD 20899, USA*

Abstract. With the introduction of soft body armor in the 1970s, methods for certifying armor systems were also developed. Roma Plastilina Clay #1 (RP1) was chosen from several clay composites, foams, and gels and continues to be used as the ballistic witness material for back face deformation of soft body armor. Unfortunately, over the decades since RP1 was adopted, changes by the manufacturer to RP1 have forced ballistics researchers to heat the composite to keep it within the specification developed in the 1970s. There is now a desire in the soft body armor testing community to replace the current material with new clay composites or other materials which do not require thermal treatment prior to use. To support that effort a proper and complete characterization of the material properties of RP1 is needed. Mechanical and thermal properties of RP1 were studied through small amplitude oscillatory shear (SAOS), large amplitude oscillatory shear (LAOS), and differential scanning calorimetry (DSC). Rheological characterizations of RP1 through SAOS have confirmed anecdotal experience by users, that the clay composite softens as it is "worked" and slowly stiffens as it rests. Using small strains the mechanical properties can be observed without perturbing the system (0.007 % strain and 0.07 % strain). Higher strains result in time dependent mechanical properties (0.7 % strain) and recovery of mechanical properties can also be observed by applying the small strain post "working" of the material. Upon heating, the clay composite softens, prior work-history is erased, and the composite undergoes a melting transition. Continuing mechanical characterizations into the LAOS or non-linear region, RP1 is a shear thinning material (modulus decreases with increasing strain) at all measured temperatures and transitions from a transient network to a viscous liquid when melted. The culmination of these experiments indicates a material with a time, temperature, and work-history dependent (thixotropic) nonlinear mechanical response. Ideal replacement room-temperature ballistic witness materials should have a similar nonlinear response to the heated RP1 without work-history/time dependent material properties. In the interim, understanding the work history/time and temperature dependent properties will help guide RP1 users in developing procedures to mitigate these undesirable properties. The mechanical and thermal analysis and comparisons to "used" ballistic witness RP1 and proposed room-temperature clays will also be discussed.

1 INTRODUCTION

Roma Plastilina clay #1 (RP1) has been the ballistic witness material of choice in the United States since the late 1970s. The rate dependent deformation, relative to torso surrogates, of RP1 placed it on par with ballistic gel (bovine collagen) both of which outperformed a similar but stiffer clay Roma Plastilina clay #2 (RP2) and an unnamed foam [1]. Although having a similar rate dependent deformation to ballistic gel, the plastic deformation of RP1 resulted in a permanent record of the ballistic event, eliminating the need for complicated and expensive experimental setups with high speed cameras and subsequent analysis of high speed video footage required for the non-permanent deformation of gels. Disposal of clay composites such as RP1 is significantly easier than disposal of biological materials such as ballistic gels. RP1 at the time of adoption was used at room temperature, however, changes in the formulation has required armor testing labs to heat the clay (≈ 35 °C) to maintain the appropriate deformation characteristics [2-4]. This heating requirement is problematic on two fronts 1) the cost associated with heating ≈ 90 kg clay boxes is rather significant especially for high through-put ranges and 2) the deformation properties of the clay composite are now temperature (time) dependent as the block slowly cools, increasing measurement complexity. Anecdotal accounts from practitioners indicate a slow stiffening of RP1 when left undisturbed, further complicating the time dependency of the mechanical properties. These issues have lead the US Army to begin developing a room temperature alternative to the currently available RP1. However, there is little information available in the public scientific literature and although several reports are available from government and academic institutions, they are not readily accessible and the experiments tended toward applied research. None of the literature provides a basic understanding of the mechanical properties, nor how individual composite components influence those properties, thus making new composite development difficult. Small and large amplitude

[1]Official contribution of the National Institute of Standards and Technology; not subject to copyright in the United States.

oscillatory shear (SAOS/LAOS) provides a non-destructive test method with a large parameter space and rich experimental and theoretical history. Using this method, basic mechanical properties of almost any material can be studied. By coupling SAOS/LAOS experiments with differential scanning calorimetry (DSC) a more complete understanding of the ballistic witness clay composites is revealed.

2 MATERIALS & METHODS[2]

2.1 Clays

Roma Plastilina Clay #1 (Sculpture House, Springhill, NJ, USA) was purchased and used as received. Aberdeen Test Center (ATC) room temperature clay was provided by colleagues at the Aberdeen Test Center (Aberdeen, MD, USA), formulation BT18c.

2.2 Differential Scanning Calorimetry (DSC)

Differential scanning calorimetry (DSC) test were run on a Q1000 MDSC (TA Instruments, New Castle, DE, USA) using aluminum pans with hermetic lids. Temperature scans were run from -50 °C to 150 °C at 10 °C/min after equilibrating at -50 °C for 10 min, the second heating cycle is reported. Runs were performed under dry nitrogen purge in T4P mode. Temperature calibration was performed using indium and lead at the same heating rate, and heat flow was calibrated through indium. Manufacturer specified temperature accuracy is ± 0.1 °C.

2.3 Rheology/Dynamic Mechanical Analysis (DMA)

Rheological characterizations were carried out on an ARES-G2 strain-controlled rheometer (TA Instruments, New Castle, DE) using stainless steel 8 mm parallel plates and 25 mm serrated parallel plates. Wall slip was observed at moderate strains requiring the use of serrated plates. Strain sweeps were run at the "usage" temperature of each composite, 40 °C for RP1 and 30 °C for BT18c and in 10 °C increments up to 90 °C from 0.001 % strain to 1 % strain at 1 rad/s. Dynamic mechanical analyses (temperature ramps) were run from 30 °C to 80 °C at 1 °C/min, 1 rad/s, and 0.01 % strain, the second heating and cooling are reported. Long recovery time experiments were run on an ARES-LS strain-controlled rheometer (TA Instruments, New Castle, DE) with stainless steel 8 mm parallel plates. Typical error for dynamic moduli on these clay composites is ≈ 10 %.

3 RESULTS & DISCUSSION

In strain-controlled SAOS experiments, a sample is deformed under a strain amplitude (γ_0) and frequency (ω) according to $\gamma(t) = \gamma_0 \sin(\omega t)$. If the deformation is linear the measured stress (σ) conforms to $\sigma(t) = \sigma_0 \sin(\omega t + \delta)$ where δ is the phase lag. The phase lag is used to separate the in-phase or strain depend stress and out-of-phase or strain-rate dependent stress resulting in two types of dynamic moduli. The strain dependent modulus G' referred to as the storage, or elastic modulus, is a measure of the "solid" like response and the strain rate depended modulus G" referred to as the viscous, or loss modulus, is a measure of the "liquid" like response both of which are constant with increasing strain under linear deformation. A complete treatment of these rheological parameters can be found in many rheology texts [5-7]. Under most experimental conditions the clay composites (RP1 and BT18c) responded as mostly elastic solids thus the reported data is focused solely on the storage modulus (G') with the loss modulus (G") falling ≈ 1 order of magnitude lower. Using a small strain amplitude, 0.015 % strain, mechanical properties can be measured without perturbing the system. By varying temperature, through a temperature ramp, under low strain the rheometer becomes the equivalent of a shear DMA measuring thermomechanical transitions, which complement the DSC thermodynamic and kinetic transitions. From the DSC several melting transitions, which appear as peaks, for RP1 and BT18c were measured, Figure 1a. For RP1 melting peaks occurred at -6.5 °C, 50.6 °C, 79.3 °C and 116.4 °C and for BT18c only two melting peaks were observed at 71.5 °C and 116.4 °C, the overlapping melting peak at 116.4 °C may indicate a shared component. Thermomechanical transitions from DMA of RP1 and BT18c,

[2]Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose. The error bars represent one standard deviation of the data, which is taken as the uncertainty of the measurement.

Figure 1b, reveal several differences between the two composites. Again focusing on G', BT18c appears to be stiffer, higher G', over the measured temperature range (30 °C to 80 °C) and has a sharper melting transition on heating and cooling occurring near 70 °C corresponding to the DSC peak at 71.5 °C on heating and closer to 60 °C on cooling, whereas RP1 has a more continual decrease in G' occurring across the entire temperature range with no easily definable transition temperature. The continual decrease in RP1 is consistent with the broad melting peak, marked at 50.6 °C in Figure 1a which spreads from 20 °C to 60 °C. Hysteresis is also present, yet very different between the two clay composites. In the cooling cycle of BT18c, there is a significant lag in the solidification occurring ≈ 10 °C lower than melting. The hysteresis in the DMA of BT18c is attributed a slow recrystallization process brought about by the stiffness of the composite. The cooling cycle of RP1 follows along a similar path to the heating cycle at a slightly higher G' which is indicative of physical aging. The simpler DSC and sharp decrease in G' from the DMA of BT18c may indicate a simpler system compared to RP1 with multiple and broad peaks in the DSC and continual decrease of G' from the DMA.

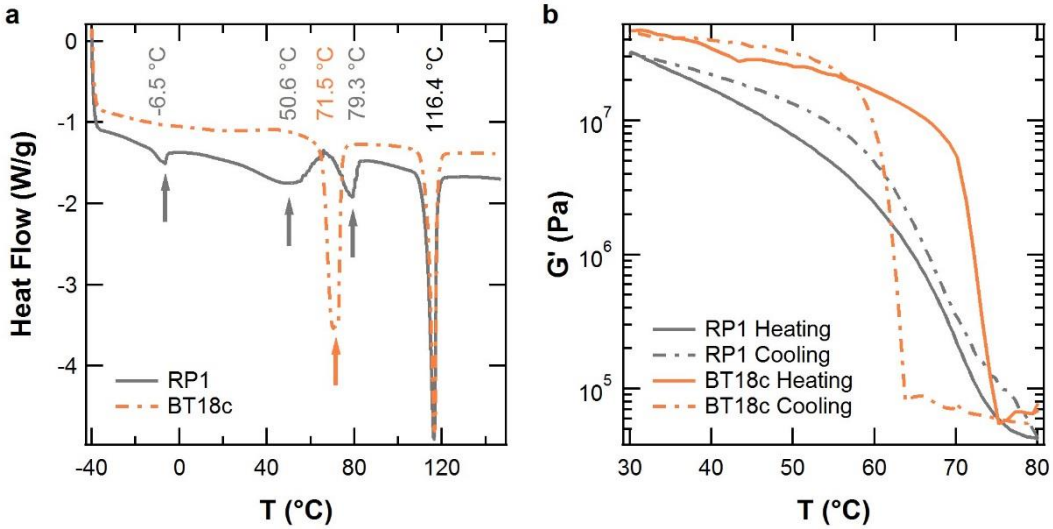

Figure 1. Thermal properties of ballistic clay composites (a) differential scanning calorimetry and (b) dynamic mechanical analysis.

Further information regarding the mechanical properties can be determined by varying the strain amplitude in SAOS experiments and general information regarding the structure can be ascertained by making measurements outside the linear region, where G' or G" are no longer constant with strain, also referred to as LAOS measurements. Strain sweeps, incremental increases in stain amplitude at fixed frequency, provide a means to define the linear (SAOS) and nonlinear (LAOS) region. In the LAOS regime there are four types of behavior, characterized by deviations in G' and G" from the linear regime [8]. In Figure 2 the normalized storage and loss modulus from strain sweeps of RP1 at 40 °C and 80 °C and BT81c at 30 °C and 70 °C exhibit two distinct types of LAOS behavior.

At the usage temperatures, 30 °C and 40 °C, G' and G" are constant until ≈ 0.01 % strain after which G' begins to decrease while G" increases to a small peak then decreases similar to G', upper curves of Figure 2a and 2b. The curvatures of G' and G" at the usage temperatures for each clay indicate a weak strain overshoot (Type III), decreasing G' with a peak in G" followed by decreasing G". The weak strain overshoot is indicative of a transient network morphology. The peak and downturn of BT18c at 30 °C are cut off due to the upper torque limit of the instrument. As the temperature is increased, to 80 °C for RP1 and 70 °C for BT18c, the peak in G" disappears and the relative shapes of G' and G" change to both decreasing as strain amplitude increases with G' deceasing at a slightly lower strain amplitude. The curvatures of G' and G" at the elevated temperatures indicate strain thinning (Type I), often seen in many viscous fluids such as polymer solutions. The higher temperatures 80 °C for RP1 and 70 °C for BT18c are approximately the lowest temperature where the weak strain overshoot disappears becoming strain thinning and correspond to a peak in the DSC for each clay composite, 79.0 °C and 71.9 °C for RP1 and BT18c, respectively.

The equilibration time chosen for the strain sweeps, while uniform for the experimental set, does not allow the sample to equilibrate. As discussed earlier the RP1 composite is known to stiffen over time, however, that equilibration time has not been quantified. By measuring the mechanical properties at a fixed frequency, strain amplitude, and regular time intervals, the recovery process can be monitored and quantified. The recovery time for a "hand-worked" sample of RP1 at 40 °C is on the order of several

days, Figure 3. After 4 d of measuring the RP1 had not completely equilibrated, however, it was found the data could be modeled with a double exponential function, Equation 1.

$$G' = G'_{\infty} + C_1 e^{\frac{t_0 - t}{\tau_1}} + C_2 e^{\frac{t_0 - t}{\tau_2}} \quad (1)$$

where G' is the measured storage modulus, G'_{∞} is the plateau value of G' at full equilibration, C_1 and C_2 are scaling constants for each exponential term, t is time, and τ_1 and τ_2 are scaling times.

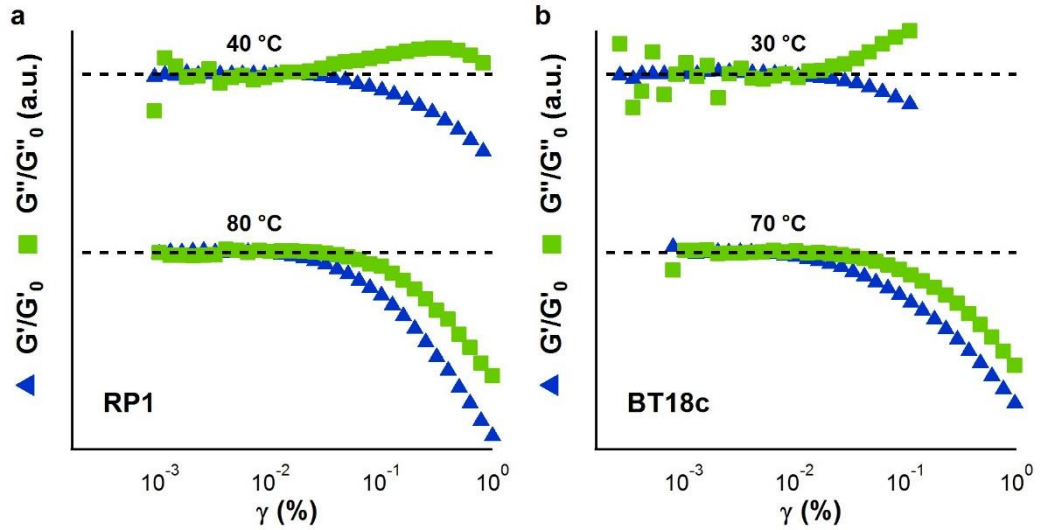

Figure 2. Oscillatory strain dependence of normalized dynamic moduli after 1h equilibration (a) RP1 at 40 °C and 80 °C and (b) BT18c at 30 °C and 70 °C. Normalized curves better illustrate the relative shapes of the dynamic moduli, G'_0 and G''_0 are defined by the respective modulus value in the linear region.

While there is no theoretical basis for the double exponential function, in fact a single exponential function fits the data sufficiently but poorly at short times, extrapolation provides a means for estimating the full recovery time. After fitting the double exponential to the recovery data and solving for $G' = 0.999G'_{\infty}$ we find the complete recovery could take 7.9 d ± 0.7 d. However, fitting the double exponential to recovery data at shorter times (i.e. 24 h or 48 h) results in a shorter total recovery predictions, which suggests that the extrapolation under predicts the total recovery time and that longer experimental runs are needed to adequately estimate the recovery time. While the results from the recovery measurements did not completely quantify the recovery time of RP1, it is clearly unreasonable for armor certification labs to wait for complete recovery of RP1.

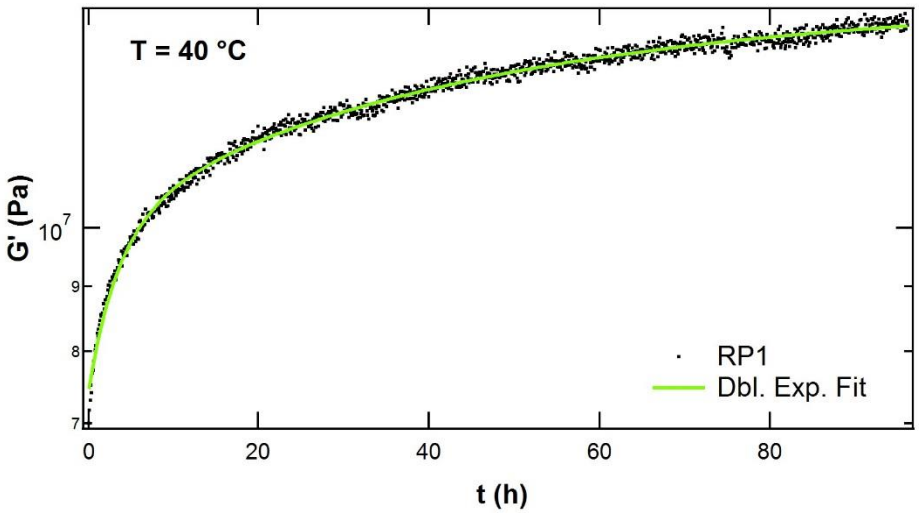

Figure 3. Long recovery time of RP1 after "working" by hand and fit to double exponential, Equation 1.

4 CONCLUSIONS

Two ballistic clay composites have been characterized using SAOS/LAOS, DMA, and DSC. Transitions in the mechanical properties from SAOS/LAOS and DMA measurements correspond well with thermal transitions from DSC. The dynamic moduli of both composites exhibit the weak strain overshoot behavior below the melting transitions occurring at 71.5 °C for BT18c and 79.3 °C for RP1, at higher temperatures the both composites exhibit strain thinning behavior. Since the dynamic moduli transition, weak strain overshoot to strain thinning, corresponds with a single, fairly narrow peak in the DSC each composite likely has one component dominating the morphology and mechanical properties in this temperature regime. The recovery time of RP1, being on the order of weeks is far too long to consider allowing the sample to reach equilibrium after mechanical working. RP1, therefore, will always be in a non-equilibrium state which, while not ideal, is acceptable so long as this is considered by practitioners and standards development committees.

References

[1] Prather R.N., Swann C.L., and Hawkins C.E., Backface signatures of soft body armors and the associated trauma effects. Technical report, Army Armament Research and Development Command, Aberdeen Proving Ground, MD, Nov 1977.

[2] Lehowicz L.G., Phase I Report on Review of the Testing of Body Armor Materials for Use by the U.S. Army: Letter Report (The National Academies Press, 2009) pp. 15-16.

[3] Lehowicz L.G., Testing of Body Armor Materials for Use by the U.S. Army–Phase II: Letter Report (The National Academies Press, 2010) pp. 14-15.

[4] Lehowicz L.G., Testing of Body Armor Materials: Phase III (The National Academies Press, 2012) pp 69.

[5] Macosko C.W., Rheology: Principles, Measurements, and Applications. (Wiley, 1994).

[6] F.A. Morrison. Understanding Rheology (Oxford University Press, 2001).

[7] J.M. Dealy and R.G. Larson. Structure and Rheology of Molten Polymers: From Structure to Flow Behavior and Back Again (Hanser Publishers, 2006).

[8] Hyun K., Kim S.H., Ahn K.H., and Lee S.J., J Non-Newton Fluid, 107 (2002), 51–65.